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Preparation and Properties of Nano-Scale Periodic Porous Carbon as Electrode Material

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Periodic nano-scale porous carbon has been prepared by the replica method utilizing a synthetic opal as a template for applications as electrode materials in rechargeable battery, super-capacitor and fuel cell. The pore size and inter-pore distance can be controlled by utilizing various synthetic opals prepared with different size of silica spheres, sintering temperature of silica opal and heat treatment of carbon inverse opal. Heat treatment temperature also influence on graphitization and on the shape of pores. Various materials such as metal phthalocyanines and metal particle such as platinum of nano-size have been successfully incorporated in the carbon inverse opals.

Properties of these nano-scale periodic porous opals have been studied and discussed in terms of applications to the secondary battery, super-capacitor and fuel cell.

KEYWORDS: porous carbon, template method, inverse opal, photonic crystal, secondary battery, super-capacitor, fuel cell

電極材料としてのナノスケール周期的多孔性炭素材料の作製とその特性

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二次電池、スーパーキャパシタや燃料電池へ応用するため、人工オパールを鋳型としてナノスケールの周期的多孔性炭素を作製した。シリカ球径やシリカ焼成温度、あるいはオパール反転炭素の焼成温度を変えることで、多孔性炭素の孔径や内部孔間の距離を制御することができる。熱処理温度は炭素の結晶化度や孔形にも影響を与える。作製した多孔性ナノカーボンは金属フタロシアニンや白金ナノ微粒子と複合化することが出来た。作製したこれらの周期的多孔性ナノスケールカーボンの二次電池、スーパーキャパシタおよび燃料電池電極としての特性を検討した。

1. Introduction

Porous carbons are materials of great interest because of their applications in electrodes of Li-ion batteries, electric double-layer capacitors and fuel cells. Nano-scale periodic porous carbons exhibit also unique characteristics as photonic crystals.

We have studied nano-scale periodic porous carbons prepared by the template method and their novel characteristics.

Inverse carbon opals with nano-scale periodic pores have been prepared by infiltrating carbons or the precursor of carbons into the interconnected voids of silica opals followed by the heat treatment and then removing silica particle by washing with HF[1)] and their characteristics have been studied[2-4)].

In this paper, precise controls of pore sizes and diameter of inter-connecting-channels between pores in the nano-scale periodic porous carbons, preparation of Pt containing nano-scale periodic porous carbons and their characteristics depending on preparation conditions are discussed.

2. Experimental and Preparation

Three-dimensional periodic structures of opals were fabricated by the sedimentation of mono-dispersed silica (SiO_2) spheres with various diameters ranging from several tens nm to several μm in diameters. These three-dimensional periodic structures of SiO_2 (synthetic opals) were heat treated to make them robust by fusing neighboring silica spheres. On the other hand, the opal was confirmed to have interconnected periodic array of nano-scale voids.

Upon introduction of various materials in the inter-connected nano-scale voids of the opals and then removing silica by treating either with HF or KOH, various inverse opals such as polymer inverse opals can be easily prepared by this template method. For example by filtration with phenol resin and then removing silica, phenol resin inverse opals can be prepared. By the heat treatment of phenol resin inverse opals at high temperatures various carbon inverse opals can also be prepared. Carbon inverse opals can be also prepared by infiltration of carbon in the interconnected voids of the synthetic silica opals in gas phase and then removing silica spheres by washing with HF.

Utilizing polymer spheres, polymer opals can also be prepared directly. For example, phenol resin opals can be prepared just by the accumulation of phenol resin spheres, and then carbon opals can be prepared by the heat treatment at high temperature.

For preparation of a pellet-type electrode, periodic nano-porous carbons were held with Ni mesh. A lithium metal plate served as the counter and reference electrodes. The electrolytes used in this study were 1M solution of $LiClO_4$ in a propylene carbonate (PC). Electrochemical measurements were carried out using beaker type cell as room temperature in an argon-filled grove box (MDB-1-B, Miwa). The cell was discharged to 0.03V vs (Li/Li^+) at a constant current and then charged to 2.5V at a constant current using a charge-discharge unit (HJ-201B, Hokuto Denko).

Pt containing nano-scale porous carbon can be prepared by introducing Pt organic complex in porous inverse carbon opals and then heat treated at appropriate temperatures.

The structure was observed by a scanning electron microscope SEM (S-5000, Hitachi) and a transmission electron microscope TEM

(H-8100, Hitachi).

The optical transmission spectrum and reflection spectrum were measured as reported in the previous papers[5)].

3. Results and Discussion

3.1 Control of voids, interconnection channel, carbon contents and periodicity

Synthetic opals were fabricated by sedimentation of the suspension of mono-dispersed SiO_2 spheres of various diameters and then sintered at 700-900oC. Figure 1 shows a SEM image of an example of the synthetic opal. This opal contains regular array of interconnected voids whose sizes are depending on the diameter of the SiO_2 sphere.

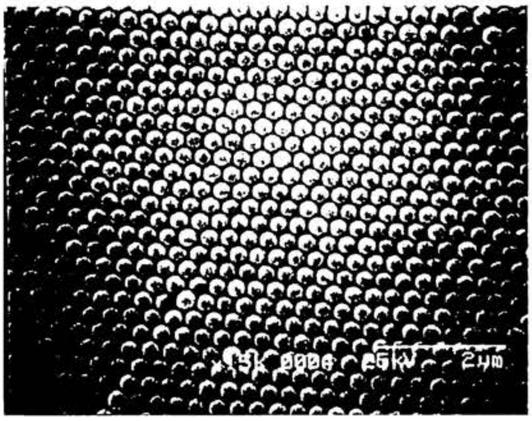

Fig.1 SEM image of the synthetic opal.
図1 人工オパールの SEM 像

Upon infiltration of various materials in the interconnected voids of the synthetic opal and then removing SiO_2 with HF, inverse opals made of various materials can be prepared. For example, SEM image of the inverse phenol resin opals prepared by this method is shown in Fig.2. This phenol inverse opal can be transformed into the carbon inverse opal by the heat treatment at temperatures higher than 600oC in Ar gas.

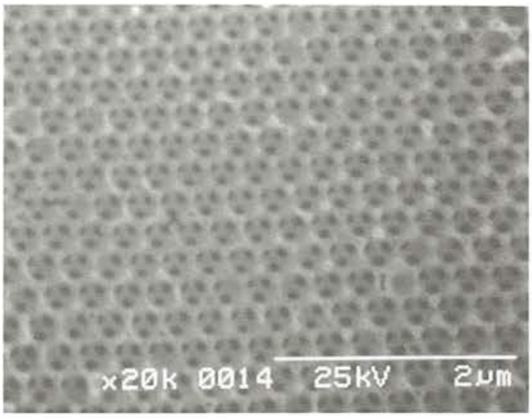

Fig.2 SEM image of the inverse opal.
図2 反転オパールの SEM 像

Figure 3 (a)-(h) shows the SEM images of porous carbon inverse opals obtained by the pyrolysis of the phenol resin inverse opals prepared from SiO_2 spheres of 1000, 550, 300, 120, 74, 43, 23 and 11 nm in diameters, for examples. As evident in these figures, there exist regular arrays of inter-connected voids whose size depends on the diameter of starting SiO2 spheres. The existence of the inter-connecting channels is also clearly indicated in SEM images.

It should also be mentioned that by changing the sintering temperature the size of voids in the synthetic opal could be controlled due to the progress of fusing of neighboring silica spheres at higher sintering temperatures. In the inverse opal made from synthetic opal sintered at different temperatures, not only the size of voids but also the diameter of the inter-connecting channel of voids can be controlled as shown in Fig.4.

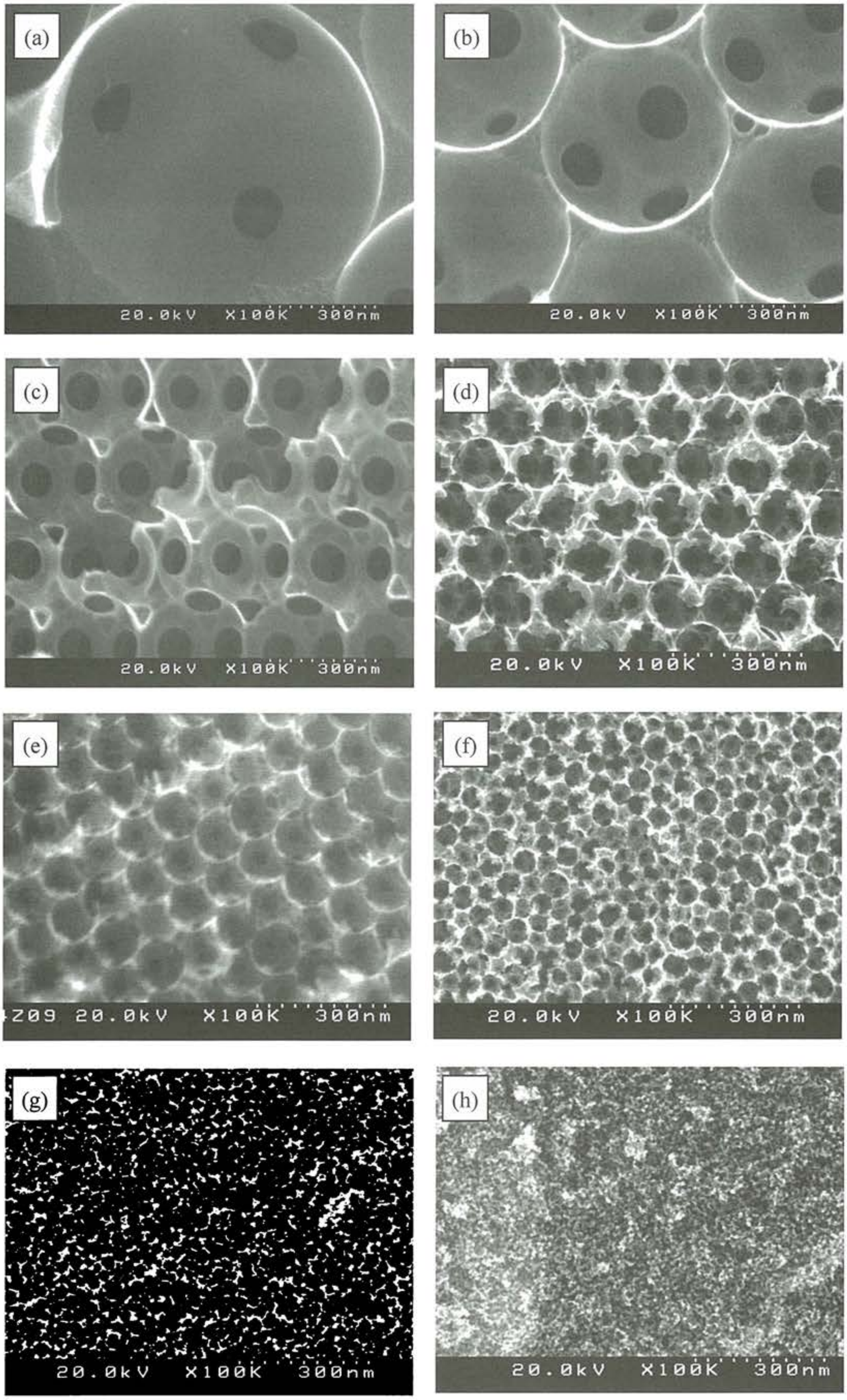

Fig.3 SEM images of carbon inverse opals pyrolyzed at 800oC. The diameters of used SiO_2 spheres are (a) 1 μm, (b) 550 nm, (c) 300 nm, (d) 120 nm, (e) 74 nm, (f) 43 nm, (g) 23 nm and (h) 11 nm, respectively.
図3 800℃熱処理多孔性炭素の SEM 像

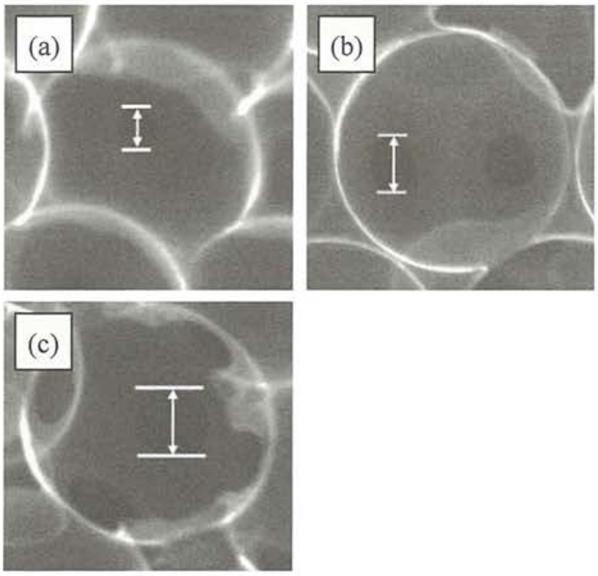

Fig.4 SEM images of the pores of the inter-connecting channel of voids in carbon inverse opals prepared at sintering temperatures of (a) 650℃, (b) 850℃ and (c) 950℃.
図4 焼結温度(a)650℃、(b)850℃および(c)950℃で作製したカーボンインバースオパールの、空隙間連結孔の SEM 像

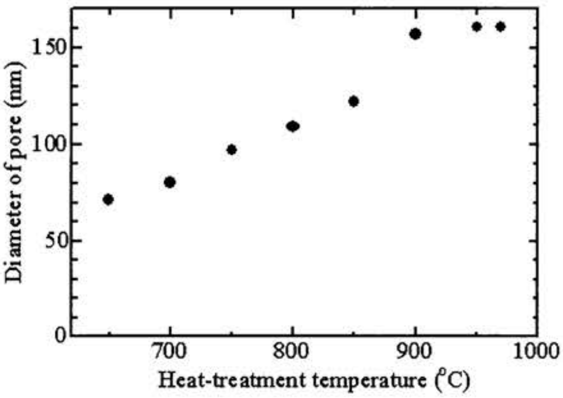

Fig.5 The sintering temperature dependence of diameter of inter-connecting pores.
図5 空隙間連結孔径の人工オパール焼結温度依存性

The inter-connecting channel in the inverse carbon opals is found to be dependent on the sintering temperature of the pristine silica opals as shown in Fig.5. The diameter of pores increase with increasing sintering temperature.

These results also indicate that the porosity, therefore, carbon content in the porous carbon can be controlled by this pre-sintering of the pristine silica opal.

Indeed, as evident in Fig.6, porous carbon

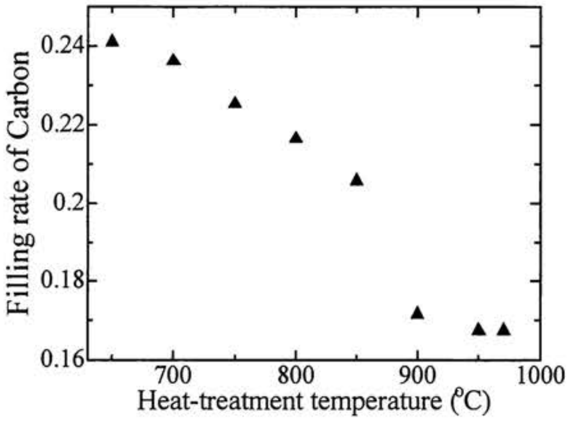

Fig.6 The sintering temperature dependence of filling rate of carbon.
図6 カーボン充填率の人工オパール焼結温度依存性

with carbon content as low as 20% can be easily realized.

Both in the opal and the inverse opal, as shown in Fig.7, sharp peaks in the reflection spectrum and dips in the transmission spectrum appear, respectively, whose wavelengths correspond to the center wavelength of the photonic band gap depending on the periodicity and the refractive index of the opal material. This fact that photonic crystal effects are observed indicates that the carbons prepared by these methods are conformed of nano-scale periodic structures.

In the reflection spectra of the inverse opals infiltrated with liquids, a sharp peak was also observed at some wavelength depending on the sort of liquids. The wavelengths of the peak in the reflection spectra were found to be dependent on the refractive index of the liquids. These effects can be interpreted in terms of the photonic band gap depending on the refractive index of the liquids.

Utilizing these phenomena, even the same alcohol, ethanol and methanol and even the concentration of the ethanol in water can be easily distinguished.

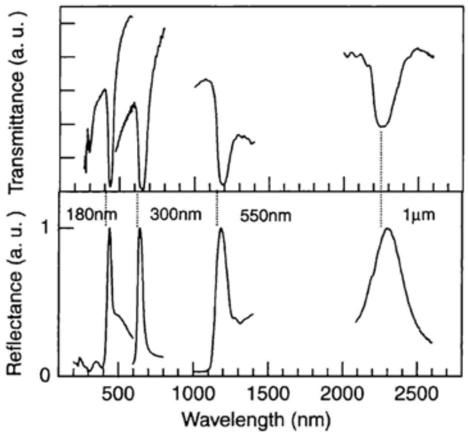

Fig.7 Transmission and reflection spectra of synthetic opals composed of various diameters of silica spheres.
図7 様々な球径のシリカ球で作製した人工オパールの透過率および反射率スペクトル

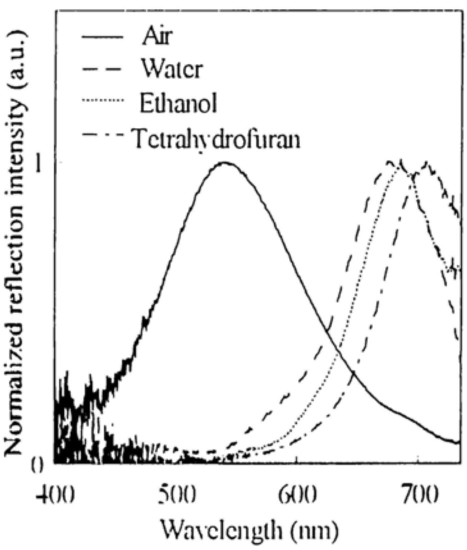

Fig.8 Reflection spectra of polymer inverse opal infiltrated with various liquids.
図8 液体を含浸させたインバースオパールの反射スペクトル

These observations clearly indicate that liquids are uniformly infiltrated in the nano-scale periodic pores in the carbon. This also clearly indicates that voids are well interconnected by channels.

These facts clearly indicate that various liquids (both hydrophilic and hydrophobic liquid) can be infiltrated in these silica opals and carbon inverse opals.

3.2 Electrochemical Properties of Periodic Porous Carbons

Dynamics of Li ions in these periodic porous structures of carbons were also studied and excellent doping and undoping characteristics were confirmed.

That is, in such periodic porous structure of carbons migration and intercalation of Li ions proceed smoothly and effectively.

Carbon materials have been used as electrodes in a lithium ion battery for use as negative electrode active materials. Many reports have shown that the charge-discharge capacity of non-graphitizable carbon heat-treated at low temperatures such as below 1100oC exceed the theoretical capacity[6-9]. The performance of lithium ion secondary batteries, such as charge-discharge capacity, speed, voltage profile and cyclic stability depend on mainly heat treatment process and carbon nano structures. The size of surface area and the dynamic behavior of the ions responsible for the characteristics of the devices are markedly influenced by material porosity.

On the other hand, the periodic nanoporous materials which consists of the material containing air-filled spheres instead of the silica spheres has been made by using the synthetic opal as the template. These materials are expected to have unique and useful properties as electrical and optical devices because it has the periodic porous nano-structure with the periodicity of the order of optical wavelengths.

Figure 9 shows the third charge-discharge profiles of a pyrolyzed periodic nano-porous carbon at HTT of 690°C. The charge-discharge test was conducted under the constant current corresponding to 300mA/g.

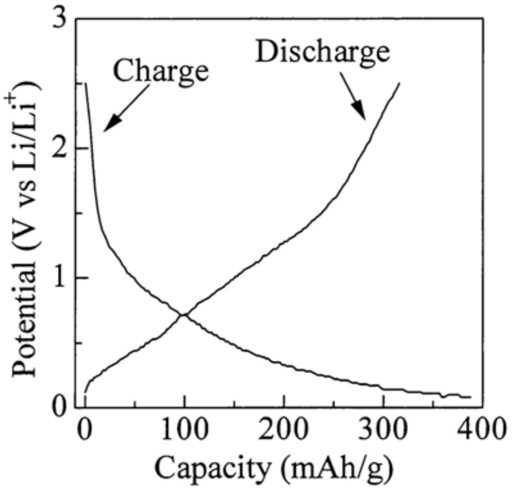

Fig.9 The third charge-discharge profiles of a pyrolyzed carbon inverse opal.
図9 熱焼成したカーボンインバースオパールの充放電曲線

The carbon electrode cell showed reversible capacity of about 315mAh/g, and indicate characteristic plateau in discharge/charge properties at about 1.0V, as well as hysteresis in voltage profile about 0.0V. From these results, it appears that the electrode made of pyrolyzed periodic nano-porous carbon shows the good stability.

Figure 10 shows that the dependence of the capacity on added metal phthalocyanines. As shown in Fig. 10, the reversible capacity has been increased up to 400 mAh/g by the addition of nickel phthalocyanine. The addition of other metal phthalocyanines, such as CuPc and ZnPc, was not as effective. From these results, it is considered that the addition of nickel phthalocyanine is most effective in enhancing the capacity.

These phenomena are assumed to be mainly due to the enhanced graphitization from catalytic effects of nickel or the increased mesopore volume accompanied by the addition of nickel, however, the precise mechanism has not been revealed at this stage.

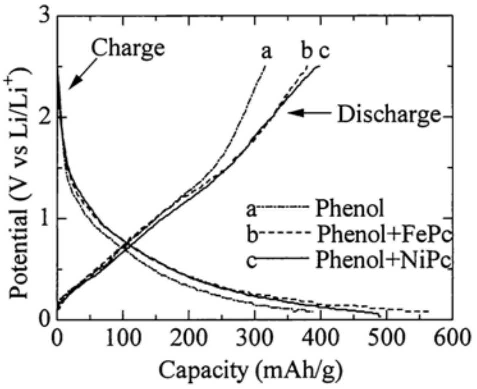

Fig.10 Dependence of the third charge discharge profiles of pyrolyzed carbon inverse opals on added metal phthalocyanines.
図10 金属フタロシアニンを添加したカーボンインバースオパールの3サイクル目における充放電曲線

Figure 11 shows the dependence of the third charge-discharge capacities of pyrolyzed samples on HTTs. The reversible capacity of pyrolyzed sample with a HTT of about 700C is the highest. That is, the charge-discharge capacity of samples can be improved by pyrolysis.

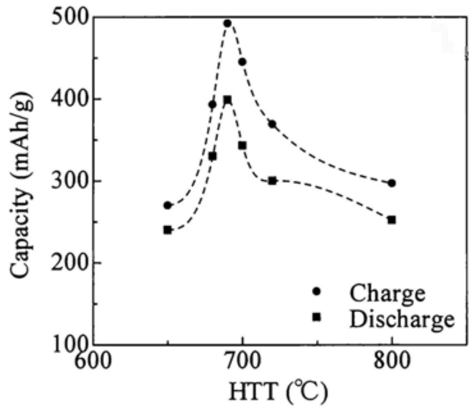

Fig.11 Dependence of the capacity on HTTs of carbon inverse opals.
図11 カーボンインバースオパールの充放電容量の熱処理温度依存性

In conclusion, we prepared periodic nano-porous carbon using synthetic opal as a template, then, we examined the electrochemical characteristics of periodic nano-porous carbon and indicated that the sample can be used as electrode active materials in rechargeable batteries.

3.3 Pt containing porous carbons for fuel cell

In fuel cells, Pt containing carbons are key material. Especially, taking the gas, liquids and ions transportaions into consideration, porous carbons containing Pt is expected to be effective in operation.

Pt containing carbons with inter-connected nano-scale void channels were prepared by infiltration of Pt organic complex such as dioleylaminedinitroplatinum for example, into porous carbons and then subsequent heat treatment as follows. At first, the obtained samples were dried at 80°C in air. And then, the samples were pyrolyzed at HTT 300°C in Ar gas to convert the organic complex to Pt particles.

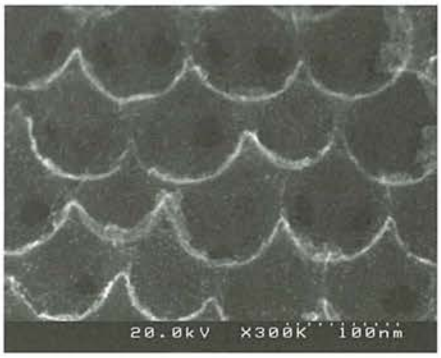

Fig.12 SEM image of Pt containing porous carbons prepared by template method from synthetic opals obtained with 74 nm
図12 Pt微粒子を担持させたカーボンインバースオパール（球径74 nmのシリカ球を鋳型に使用）

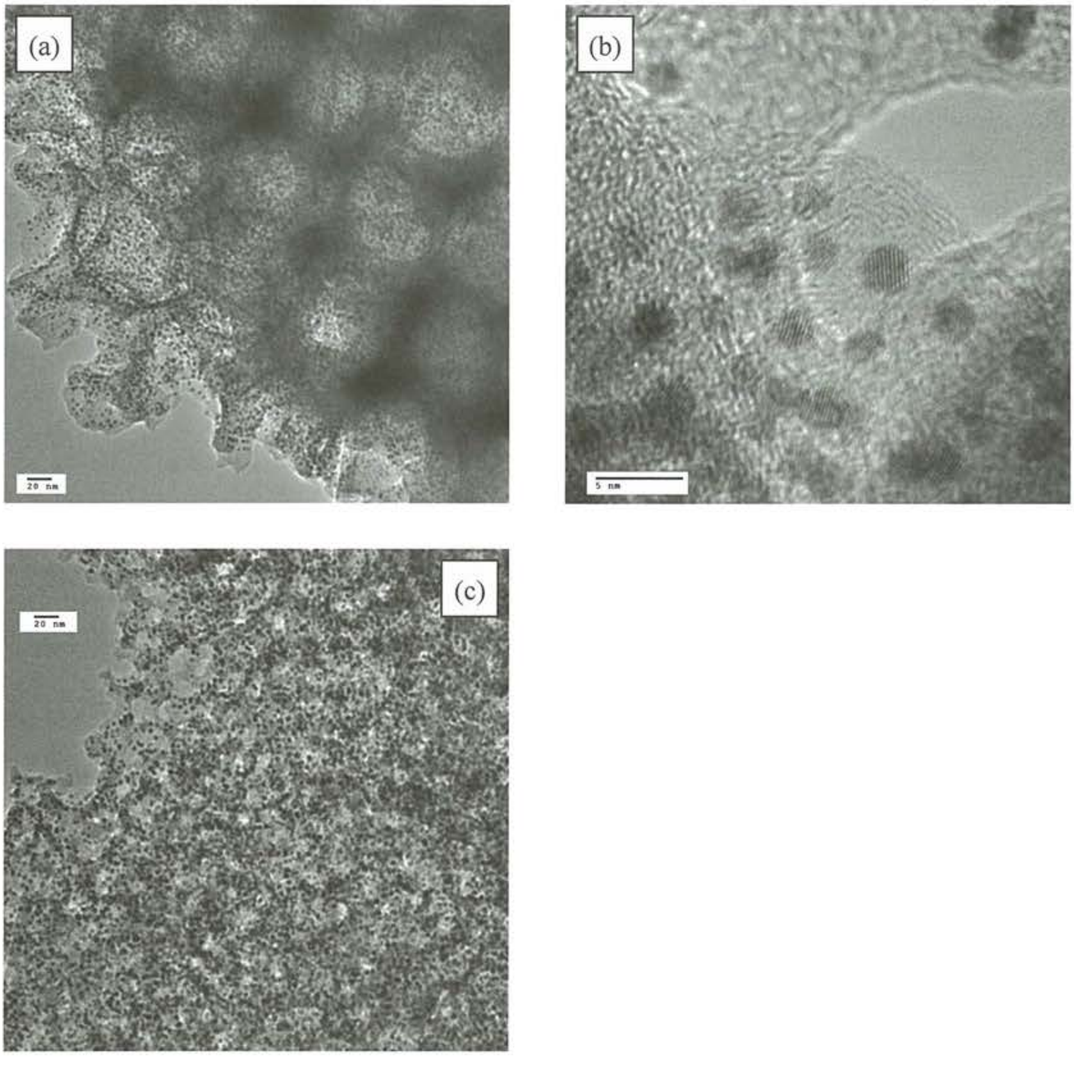

Fig.13 TEM images of Pt containing porous carbons prepared by the template method from synthetic opals obtained with 74 nm spheres (a)(b)and (c) 23 nm spheres.
図13 球径(a)(b)74 nm および(c)23 nmのシリカ球を用いて作製した白金担持多孔性炭素のTEM像

Figure 12 and 13 show SEM and TEM images of Pt containing porous carbons prepared by template method from synthetic opals obtained with 74 nm and 23 nm silica spheres.

As shown in Fig. 12, fine nano-particles, which are considered to be Pt particles, were distributed to the whole of the carbon inverse opals.

Crystal structure of dispersed particles is clearly shown in Fig. 13(b).

It should also be mentioned that in these Pt containing porous carbons Pt nano-particles are located at the inner surfaces of voids and inter-connecting channels, which means that Pt content is reduced compared with carbons containing Pt particles in bulk.

The characteristics of the Pt containing porous carbon as electrode materials in the fuel cells are now under study.

3.4 Other interesting characteristics of nano-scale periodic porous carbons

It should also be noticed that the periodic porous carbons has unique surface structures. That is, the surface is composed of periodically ordered sharp spits of needles with periodic nano-scale separations. These sharp-edged structures can be also effectively used for some applications. For example, the electron emission from such sharp edges may enhance electron emission strongly and can be utilized as emitters. On the other hand, it should be mentioned the contact between the nano-scale periodic porous carbons with other material of surface could bring various effects. Charge emission into the contacted material should be enhanced for the use of electro luminescence device and so on. It should also be stressed that the contact surface are is quite small in this case. That is, the thermal transmission through the interface should be much suppressed. In some cases, small contact area may be enough for the realization of some effects, which may be important for the saving of the material with keeping nearly the same effect.

Gas transmission, liquid transmission and ionic species transmission at the interface should be enhanced.

The large surface area in the periodic porous nano-carbons with nano-scale voids and interconnected channel suggest their use as electrodes in the super-capacitor of double layer type.

4. Summary

The present study can be summarized as follows.

1) Three-dimensional photonic crystals such as opals and inverse opals with the regular array of inter-connected voids have been prepared. The size of voids and the diameter of the connecting channels can be controlled precisely.

2) Carbon inverse opals with three-dimensionally periodic structures were prepared by pyrolysis of phenol resin infiltrated opals obtained by sedimentation of silica spheres of 1000nm, 300nm, 120nm, 74 nm, 43nm, 23nm and 11nm in diameters.

3) Upon increasing temperatures of the pyrolysis, pore sizes and therefore inter-pore distances decreased and graphitization progressed. However, graphitization was also strongly influenced by the size of voids.

4) By changing sintering temperature of the original silica opals, the diameter of interconnection void channels between neighboring pores in carbon inverse opals can be controlled.

5) Dynamics of Li ions in these periodic porous structures of carbons were also studied and excellent doping and undoping characteristics were confirmed, which suggests that the periodic porous carbons with interconnected channel can be excellent candidate as electrode materials in Li ion batteries.

6) Pt can be incorporated in the nano-scale periodic porous carbons, which will be useful for fuel cells.

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